Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.23034

132 (2018) 10–19
November

Cleaning research on reverse osmosis membranes depth-fouled by transition metal oxides and silicates in ultrasound-assisted organic acids

Yong-Sheng Li [a,*], Xia-Qing Wang[a], Xiu-Feng Gao[b]

[a]*School of Chemical Engineering, Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu 610065, China, email: li-yongsheng@scu.edu.cn; lysgxf2005@qq.com. (Y.-S. Li), 884354472@qq.com (X.-Q. Wang)*

[b]*West China School of Preclinical and Forensic Medicine, Sichuan University, No.17 People's South Road, Chengdu 610041, China, email: xiufengg@163.com (X.-F. Gao)*

Received 13 February 2018; Accepted 18 August 2018

ABSTRACT

At present in the world, the waste reverse osmosis membrane (WROM) after depth-fouled are enormous in quantity, this not only increases cost of ROM in use, causes the resource waste, but also bring on serious environmental problems. To realize performance recovery and recycling of WROM, a system that can monitor ultrasound-assisted chemical cleaning process was designed. Therewith, using the system, cleaning effects for WROM depth-fouled by transitional metal oxides and silica as well as a small amount of organic matters were evaluated under various circulating flow states of pure water, ultrasonic water or organic acids and compounded liquid. The research results manifested that, in 50 kHz of ultrasonic frequency and 0.64 W/cm^2 of sound intensity, if only alone used tartaric acid, oxalic acid and citric acid to clean WROM, total defouling ratio for inorganic and organic pollutants could respectively reach about 70%, 83% and 85%, if adopted the mixing solution containing 6.9 g/L tartaric acid and 1.1 g/L Na$_4$EDTA, the defouling ratio reached to 96% which was the best synergistic effect in cleaning. The obtained results in the research can be used in the industrial online cleaning for depth-fouled ROM or resuscitating for WROM in water treatment industries.

Keywords: Reverse osmosis membrane; Organic acid; EDTA; Ultrasound-assisted; Defouling ratio; Contaminant

1. Introduction

Currently, reverse osmosis membrane (ROM) has been widely used in treatments of textile wastewater [1–3], urban wastewater [4–6], seawater [7–10] and brackish water desalination [11–13], preparation for pure water [14] and purification of edible solutions [15,16]. In the use of ROM, contaminants will lead to significant degradation in its performance [17]. If the contaminants in ROMs could not be removed timely, lots of ROMs would gradually lose the efficacy and were discarded. This will not only increase the cost in the ROM application, but also result in the resource waste and increase the environmental load, therefore, recovering the flux of the yielded water and desalting properties of the contaminated or disused ROMs have also become one of the main contents in the current research on ROM [18–20].

The cleanings for the contaminated ROM commonly uses chemical [21–24] or physical means [25]. The chemical cleaning is to achieve this purpose that the fouling in ROM is removed via chemical reactions, dissolution, emulsification, dispersion and adsorption of chemicals, in which the common reagents are acid, alkali, metal chelating agent, surfactant, oxidant, cyclodextrin, etc. [26–28].

The common method employed in the physical cleaning is ultrasonic, which has been widely used in food industry [29], textile industry [30], bio-fuel [31], sewage treatment [32], medical treatment [33], etc. Because the acoustic streaming, micro flow and internal jet of ultrasonic [34] can effectively remove the ROM fouling, our team also began to evaluate the cleaning effect of ROM by using ultrasound to assist chemical cleaning [35,36].

---

*Corresponding author.

Literature indicated that [37], the use of ultrasound in cleaning the nano-filtration membrane could efficaciously dislodge the fouling and doesn't introduce new pollutants, in which cleaning steps was simple. But, there were also deficiencies in the ultrasound cleaning, namely, its cleaning effect is limited, the energy consumption is large, and it could cause damage of the membrane if the ultrasonic time was over-long and the intensity was over-strong [38].

In addition, the literature also proved that [39] when ultrasonic was used in the producing-water process of ROM, adsorption rate of fouling on the ROM surface could be reduced to a certain extent, and only using the ultrasonic to clean, the producing-water flux of ROM could only recover to about 10% of the new membrane performance [40], and only using the chemical cleaning, the membrane flux could only recover to about 70% of the new ROM, but the membrane flux could effectively restore after the combination of two methods, so, combining the physical ultrasound with the chemical cleaning should be the best. Utilizing "physics plus chemistry" cleaning can synthesize advantage of two methods, not only can improve ROM's cleaning effect, but also can lower the energy consumption and avoid the damage of ROM.

Therefore, the topic has conducted the research on "physics plus chemistry" cleaning method, in which the cleaning effects of waste ROM were evaluated by using tartaric acid (HTA) and HTA/Na_4EDTA compounding reagent under the ultrasound-assisted, respectively.

HTA, which contains two hydroxyl and carboxyl ($C_2H_2(COOH)_2(OH)_2$), can complex with all kinds of metal ions which was dissolving in the cleaning fluid, and its carboxyl can also take place the chemical reactions with the compounds of metal oxide, hydroxide and the salts of strong alkali weak acid on the ROM surface to remove inorganic scale on the membrane. Besides, HTA is an organic weak acid, which has only little corrosivity on the metal pipes and other power equipment in the related system. Considering that it may not be very effective to use single HTA to the cleaning of the deep-polluted ROM, so the organic chelating reagent of ethylenediaminetetraacetic acid disodium salt (Na_4EDTA) was also selected to compound with HTA in this research. Na_4EDTA can effectively remove divalent and trivalent metal cation and can also complex with Ca^{2+} and Mg^{2+} in various pH ranges and various concentrations [41]. In order to further improve the cleaning efficacy of the compound reagent, its cleaning capacity to waste ROM was also examined in applying the ultrasound.

2. Experimental and methods

2.1. Apparatus and reagents

The main equipments used in this research were a SG7200HB-I type supersonic cleaner (Shanghai, Guante), an UV-1800PC type spectrophotometer with a flow-through cell (Shanghai, Meipuda), a L1600300 type Fourier infrared spectrometer (US, Perkin Elmer), JSM-7500 type SEM (Japan, JEOL), a X-MAX50 type x-ray energy spectrometer (English, OXFORD), a DJS-1 type conductivity electrode and CM-230 type conductivity meter (k = 0.933, Hebei, Keruida), a JC202 type thermostat dryer (Shanghai, Chengshun), a CP224S type electronic balance (Sartotius, Germany), a KL-UP-IV-10 type ultrapure water system (Chengdu, Kangning) and a KH206 type paperless recorder (Xiamen, Kehao). An OH-type strong anion resin column (i.d. 3.0 mm, length 100 cm) was homemade [42], in which 0.5472 g of the strong anion resin (Amberjet-4200OH) from ROHM HAAS was filled and the resin particle size was 0.3–0.45 mm.

Chemical reagents (AR) concerned in the research were tartaric acid (HTA), NaOH, HCl, ethylenediaminetetraacetic acid disodium salt (Na_4EDTA), hydrochloric acid, potassium hydrogen phthalate (PHP) and sodium hydroxide, which were bought from Chengdu, Kelon Co. Ltd.

2.2. Reagent preparations procedure

2.2.1. 1.0 g/L of potassium hydrogen phthalate standard solution

After drying at 120°C to the constant weight, 0.500 g potassium hydrogen phthalate (KHP) was weighed to put in a beaker and dissolved by ultrapure water, and then the solution was transferred to 500-mL volumetric flask and diluted to the maker with water. The solution can be diluted to series of KHP working solutions as needed.

2.2.2. 1.2 mol/L HCl stock solution

100 mL concentrated HCl (12 mol/L) was taken to decant into a beaker and diluted by 900.0 mL ultra pure water. The solution can be diluted to series of HCl working solutions as needed.

2.2.3. 25 mmol/L NaOH stock solution

1.0 g of NaOH was weighed to put into a beaker and dissolved by ultrapure water, and then the solution was transferred to 1000-mL polyethylene volumetric flask to dilute to the maker. The solution can be diluted to series of NaOH working solution as needed.

2.2.4. Succinic acid solutions for cleaning

2, 4, 6, 8 and 10 g of succinic acid were taken respectively to move into different beakers and dissolved by 1000 mL ultrapure water to prepare 0.2, 0.4, 0.6, 0.8 and 1.0% (*w/v*) of cleaning solutions.

2.2.5. Tartaric acid solutions for cleaning

2, 4, 6, 8 and 10 g of tartaric acid were weighed respectively to put into different beakers and dissolved by 1000 mL ultrapure water to prepare 0.2, 0.4, 0.6, 0.8 and 1.0% (*w/v*) of cleaning solutions.

2.2.6. 0.6% (w/v) NaOH cleaning solution

6.0 g of NaOH was weighed to put into a beaker and dissolved by 1000 mL ultrapure water, which was used as cleaning solution.

2.2.7. 0.2% (w/v) oxalic acid cleaning solution

2.0 g of NaOH was weighed to put into a beaker and dissolved by 1000 mL ultrapure water.

2.2.8. 0.5% (v/v) phosphoric acid cleaning solution

5.0 mL phosphoric acid was taken to decant into a beaker and diluted by 995 mL ultrapure water.

2.2.9. 0.6% (v/v) acetic acid cleaning solution

6.0 mL acetic acid was taken to decant into a beaker and dissolved by 994 mL ultrapure water.

2.2.10. 1.0% (w/v) citric acid cleaning solution

10 g of citric acid was weighed to put into a beaker and dissolved by 1000 mL ultrapure water.

2.2.11. 0.24% (v/v) HCl cleaning solution

2.40 mL HCl was taken to decant into a beaker and diluted by 997.6 mL ultrapure water.

2.2.12. 3% (v/v) HCl regeneration solution

15 mL of concentrated HCl was taken to decant into a beaker and diluted by 485 mL ultrapure water, which was used for regenerating the strong cation exchange resin.

2.2.13. 4% (w/v) NaOH regeneration solution

20 g of NaOH was weighed to put into a beaker and dissolved by 500 mL ultrapure water, which was used for regenerating the strong anion exchange resin.

2.3. ROM specimens and defouling ratio calculation

The size of used ROM specimens and the specimen preparation were referenced [35]. In the research, the mass (m_{new}) of a new ROM specimen after the constant weight was 485.2 mg, which was used as the comparison. The formula for calculating the defouling ratio was as follows:

$$R_p = \frac{m_p - m_{clean}}{m_p - m_{new}} \times 100\% \quad (1)$$

where m_p is the total mass of the ROM specimen which is carrying contaminant (mg), m_{clean} is the mass after cleaning the ROM specimen (mg), and R_p is the defouling ratio (%) on the ROM surface.

2.4. Cleaning procedure and monitoring system for ROM specimens

The ultrasound-assisted chemical cleaning (UCC) system for ROM specimens was used in this experiment as Fig. 1. Firstly, the detection process of cleaning inorganic contaminant on the ROM membrane surface is operated to obtain the blank signal, namely, the peristaltic pump (0.60 ml/min) started, the cleaning liquid in a cleaning container located in the ultrasonic cleaner is pumped successively

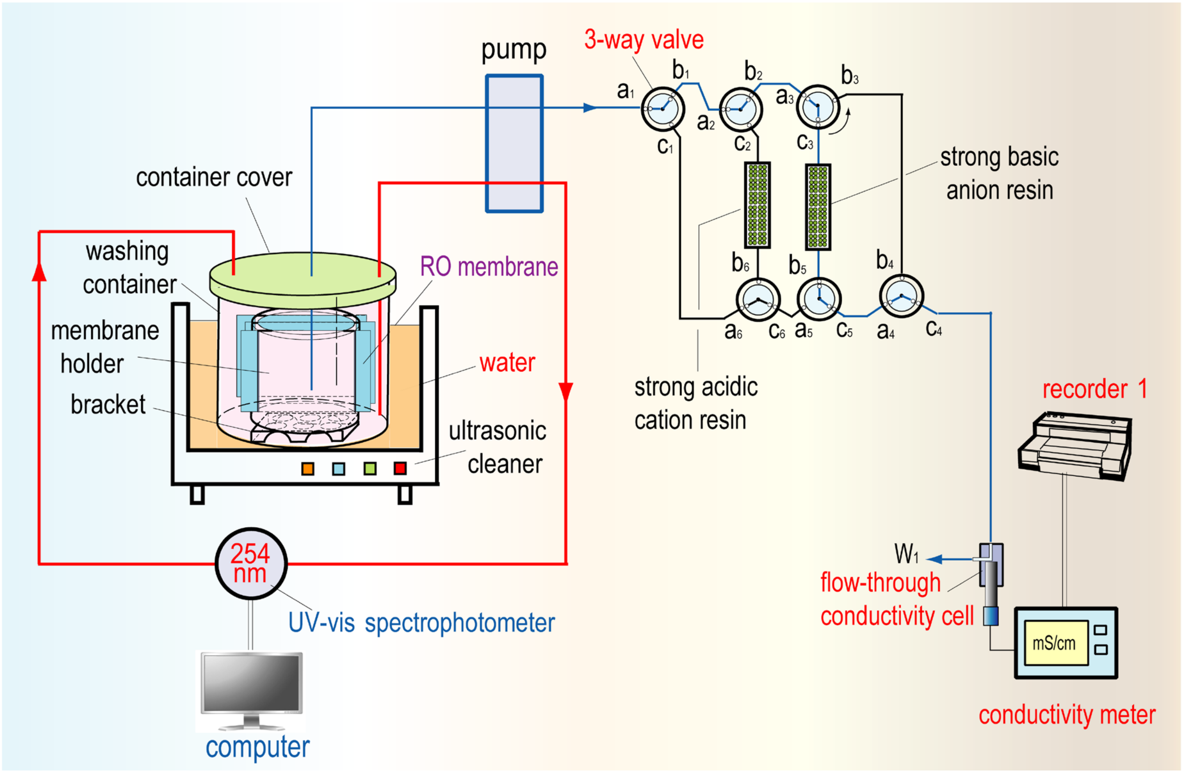

Fig. 1. An ultrasound-assisted chemical cleaning and monitoring system for cleaning the waste reverse osmosis membrane.

into a_1/b_1, a_2/b_2, a_3/b_3 and b_4/c_4 of three-way switch valves, and flowed into the flow-through conductivity detector to waste (W_1), and the blank conductivity of the cleaning liquid is obtained, which is recorded via the recorder.

When the ROM washing started, the cleaning liquid would be pumped into the three-way valves of the a_1/b_1, a_2/c_2 and a_3/c_3 ways, the strong-anion resin column, the three-way valves of the b_5/c_5 and a_4/c_4 ways, and into the conductivity detector. At this time, the conductivity meter would give the conductivity signal related to inorganic pollutants washed off from the membrane surface.

Since the resin column will fail after operating a certain time, there is a regenerative process for the resin column in the system. Here, the regenerating for the strong-anion resin was used as an example, namely, under the aspiration action of the pump, the 4% NaOH solution was pushed into a_1/c_1, a_6/c_6 and a_5/b_5 ways of three-way valves, the resin column, c_3/b_3 and b_4/c_4 ways of three-way valves, and went into the conductivity detector to W_1. After finished the regeneration, the resins in the column were flushed continuously with the pure water until the conductivity at the resin column outlet closed to that of the pure water (<1.2 mS cm^{-1}).

The liquid flow (5.0 ml/min) for monitoring the cleaning liquid absorbance (A) was cyclic, in which all the liquid flow to be detected will flow back to the cleaning container, meanwhile, the spectrophotometer will give the absorbance value, which is displayed and recorded via the computer.

2.5. Principle of monitoring inorganic contaminant in cleanout liquid

When inorganic contaminants on the ROM surface were dissolved into the cleanout liquid of the UCC system, it will cause the increase in conductivity of the cleanout liquid. So in the cleaning process, monitoring the conductivity change over time can indirectly obtain information on the inorganic content cleaned from the ROM surface, and the information can be used for the judgment of ROM's cleaning effect. But organic acids itself are very large in conductivity which will result in forming the higher blank value, and the conductivity value of the inorganic contaminant cleaned off from the ROM surface is relatively smaller than that of the cleanout liquid of the organic acids, so under the high blank conductivity, it was very difficult to directly distinguish why conductivity. As a result, the strong-anion exchange-resin column (ROH) was inserted into the monitoring system to attain this purpose that lowered the blank conductivity of organic acids itself in the cleanout liquid. HTA was first selected in various organic acids as research object, so about the ion-exchange principle between organic acids and the resin [42], taking HTA for example, explanation was as follows:

Tartaric acid ionization: $\mathrm{HTA} \rightarrow \mathrm{TA}^- + \mathrm{H}^+$ (2)

HTA solution passing the anion resin column:
$\mathrm{ROH} + \mathrm{TA}^- \rightarrow \mathrm{RTA} + \mathrm{OH}^-$ (3)

H^+ (from HTA) + OH^- (from anion resin) →
H_2O (into the conductivity cell) (4)

where TA^- represents the tartaric acid root.

It can be known that from the ion-exchange reaction formulas 2–4, if TA^- coming from HTA in the cleanout liquid was flowed through the strong anion resin column, the ion-exchange reaction would be happened between TA^- and OH^- which belonged to the anion resin, in which OH^- reacted with H^+ to generate H_2O. So after HTA passed through the anion resin column, the blank conductivity obtained by us was close to zero (pure water conductivity), in this way, the goal of lowering the conductivity of organic acids itself as the cleanout liquid was achieved.

If the inorganic contaminants from the ROM surface were cleaned off by HTA, the HTA solution conductivity would increase, namely, cation in the HTA solution did not conduct the ion-exchange reaction as passing through the anion resin column [45] and directly flowed into the conductivity detector to cause the conductivity increasing. Without any doubt, the anions in these inorganic contaminants want make ion-exchange reaction with the anion resin via the resin column to release the equal amount of OH^-, which also caused the conductivity increasing when it flowed into the detector. Therefore, in the UCC system, inserting the anion resin column can obtain the conductivity curve, related to the content of the inorganic contaminants in the cleanout liquid from the ROM surface, finally the cleaning effect of the cleanout liquid can be evaluate according to the curve.

2.6. Principle of monitoring organic contaminant in cleanout liquid

Literatures [43,44] manifested that PHP solution has the maximum absorption at 254 nm, where all organic contaminant almost existed the absorption, so in this study, PHP was used as the standard to represent organic contaminant, and absorbance value of the cleanout liquid was monitored at 254 nm to determine therein the content of organic contaminant which was washed off from the ROM surface in real time.

3. Results and discussion

3.1. Performance measurement for the resin column

The OH-type resin column used in the UCC system was to reduce the blank conductivity of organic acids and to get the conductivity curve only related to inorganic contaminant from ROM, so ion-exchanging reproducibility for the column will directly affect accuracy of inorganic contaminants measured. Therefore, the reproducibility test was conducted, in which the involved estimation indexes were the working exchange capacity (E_w), equilibrium exchange capacity (E_q), total exchange capacity (E_t) and utilization ratio (h) of the column [46]. So, 0.4% HTA was used as the test sample and was continuously pushed by the pump into the resin column to carry out three repeated experiments, in which the obtained results were $E_w = 1.14 \pm 0.05$ mmol/g, $E_q = 2.28 \pm 0.05$ mmol/g, $E_t = 3.41 \pm 0.07$ mmol/g, h = 50.14%. From the deviation of these data, it can be seen that the exchange capacity and utilization ratio of the strong anion resin filled in the column were all in reasonable range. In addition, the relative standard deviation (RSD) obtained by calculating these parameters was less than 4% which also indicated that the reproducibility for the column ion-exchanging was very good.

3.2. Linearity of flow systems to detect organic and inorganic contaminants

Repeated detections were conducted at 254 nm by using PHP solutions (10 and 30 mg/L) as testing samples, in which the obtained results were $A_{10} = 0.137 \pm 0.0005$ and $A_{30} = 0.406 \pm 0.001$ (n = 11). Subsequently, the linear examination was also carried out with different PHP standard solutions, and result displayed that there was a good linear correlation in the range 0–30 mg/L ($A = 0.014c_{PHP}$, r = 0.9995).

After that, with the HCl solution as the test sample, correlationship between the conductivity and the concentration of the electrolyte was examined, in which the result was $S_c = 367.59c_{HCl} + 13.978$ (r = 0.9997) in range of 0–4.8 mmol/L. And then reproducibility for the conductivity eleven were detected by 1.20 and 4.80 mmol/L HCl, in which the mean conductivity acquired was 453.4±1.4 μS/cm for 1.20 mmol/L and 1817.5±2.2 μS/cm for 4.80 mmol/L, respectively, and RSDs were 0.32% and 0.12%, respectively.

3.3. Surface analysis with ROMEDX and XRD apparatuses

In the research, the ROM specimens were the waste depth-polluted CPA2-4040 type polyamide ROMs (WROM), which were used in the wastewater treatment system. Fig. 2 was the obtained EDX curve related to WROM, and the relative element content was also acquired by using the energy dispersive *x*-ray detector. It was observed that contaminants on WROM mainly included 2.25% calcium, 1.85% silicate, 4.3% aluminum, 46.91% Mn, 8.54% iron, 1.84% barium and 34.31% oxygen. By contrasting with the standard graph, we knew that constituents in the contaminant on the WROM surface may be made of transition metal oxides from iron and manganese, silica, barium fluoride, and trace organic matter.

3.4. Cleaning contaminant on the ROM surface with HTA

3.4.1. Effect of HTA concentration on ROM cleaning

In this experiment, the concentration effect (0.2, 0.4, 0.6, 0.8 and 1.0%, *w/v*) of HTA as the cleanout liquid on ROM cleaning were evaluated under such conditions of 50 kHz ultrasonic frequency and 0.64 W/cm^2 sound intensity [35]. The specific operation was as follows: when ultrapure water was flowing circularly into the UCC system and the two baselines as water blanks (B_w) had tended to stable in two detectors, the pump stopped, some ROM specimens were placed in the cleaning container, then the pump again run to carry out the process of the water circulation cleaning (C_w), in which magnitude of ultrapure water conductivity (S_c) was to reflect the amount of inorganic contaminants washed from the ROM surface, and the absorbance (A) was to reflect the washed amount of organic fouling on the ROM surface.

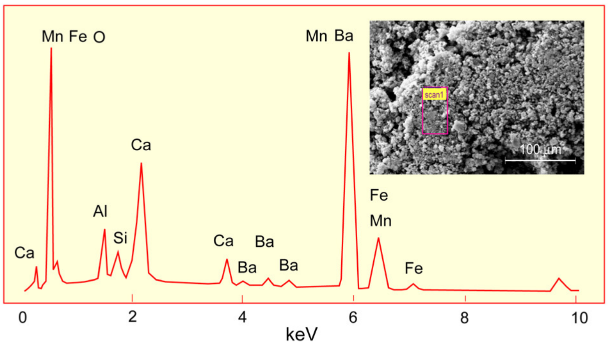

Fig. 2. Analyzing for elements on deeply fouled ROM surface.

When the conductivity and absorbance in the C_w process were no longer changed, the supersonic cleaner was powered on to conduct next process of the ultrasonic-assisted water circulation cleaning (U_w), in which the conductivity and absorbance changes were recorded in accordance with a certain period. As the responding signal in the U_W process had tended to stable, the ROM specimens were taken out, and the HTA solution was substituted for ultrapure water to circulate within the UCC system and to obtain two blank values of tartaric acid (B_A). And then, the ROM specimens were again put into the container to conduct the circulation cleaning of HTA (C_A) and the ultrasonic-assisted HTA circulation cleaning (U_A), in which the conductivity and absorbance were also recorded simultaneously. After finished these processes, the some real-time monitoring curves were obtained as shown in Figs. 3a, b. The cleaned ROM specimens were taken out from the container to weigh after drying for 25 min to do the constant weight at 40°C [35].

Fig. 3a shows that in processes of C_W and C_A, the trending of the conductivity and absorbance curves was all firstly rising then no longer change, this suggested that ultrapure water or HTA could remove the partial inorganic and organic contaminants on the ROM surface, and efficiency of the HTA cleaning was higher than that of ultrapure water. In going into the U_W process, the conductivity on the basis of the C_W process again continued to rise and then tended to stable, this phenomenon indicated that after applied ultrasonic, the residue inorganic contaminant on the ROM surface was further cleaned away. When going into the U_A process, the conductivity related to the ROM specimens soaked in 0.2–1.0% HTA solutions again significantly was risen, which showed that ultrasonic further promoted the cleaning effect of HTA, but only using HTA without ultrasound to clean the ROM was limited in the effect. Besides, when the HTA concentration was in 0.4–0.8% range within the UCC system, the recorded conductivity curve of cleaning the inorganic contaminant on the ROM surface was no longer change, which demonstrated that in this C_A process, the high concentration of HTA had been able to completely clean off the inorganic contaminant on the ROM surface without ultrasonic.

Therefore, it can concluded that, as the HTA concentration was different, its cleaning effect was also different for inorganic contaminant on the ROM surface, and effect of 0.2% HTA for cleaning was the worst, but as the HTA concentration was in the range of 0.4–1.0%, inorganic contaminant on the ROM surface can be cleaned off completely under the premise that did not applied ultrasound.

Fig. 3b shows that changing of the absorbance was very small in the C_W process, which attested that ultrapure water cannot wash off the organic contaminant on the ROM surface. In going into the U_W process, the corresponding absorbance had the remarkable increase, this manifested that ultrasound could effectively promote the cleaning of organic contaminant on ROM. In the C_A process, the absorbance again increased significantly, indicating that HTA had obvious effect on cleaning the organic contaminant on the ROM surface. When entering the U_A process, the increasing in absorbance was more prominent and the increasing trend was greater. Further, Fig. 3b also shows that the HTA concentration had a great influence on the cleaning the organic contaminant on the ROM surface, and the absorbance was the maximum as the HTA concentration was 0.8%. So 0.8% HTA was deemed to the best concentration for the cleaning.

Under conditions in Section 2.3, according to the mass changes before and after cleaning the ROM specimens, defouling ratios of the ROM in different HTA concentration were obtained by calculating with formula 1, and the related results were shown in Fig. 3c. The total influence of the HTA concentration on the cleaning of inorganic and organic fouling on the ROM surface was that when the HTA concentration was 0.8%, the defouling ratio was the largest and reached to 70%. Therefore, the concentration was selected as 0.8% to use in the compounding liquid.

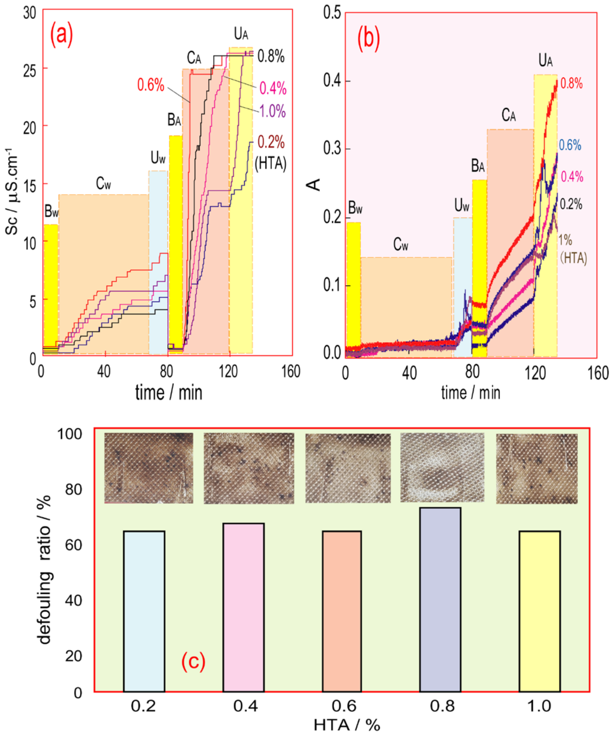

Fig. 3. Effects of different HTA concentrations on inorganic (a) and organic contaminants (b) as well as defouling ratio (c) of ROM surfaces in different cleaning processes.

3.4.2. Effect of HTA acidity on cleaning ROM's contaminant

The literature [41] demonstrated that the cleaning effect can be improved by adjusting pH of oxalic acid solution with ammonia water. Therefore, this experiment also tried to add ammonia (15 mol/L, 20–35%, *w/v*) into 0.8% HTA solution and to investigate the compounding effect of the cleanout liquid acidity on the ROM cleaning.

On the grounds of the change curve from the conductivity in Fig. 4a, the larger the pH value of HTA, the worse the effect of cleaning the inorganic contaminant, namely the worse the compounding effect for the both. In the light of the absorbance changing in Fig. 4b, we also knew that the higher the pH value in the mixture solution, the worse the effect of cleaning the organic fouling, i.e. there was not the good compounding effect between ammonia and HTA. In addition, it can be seen that under ultrasound-assisted, the cleaning of inorganic and organic pollutants had a certain synergistic effect, and the total defouling ratio was the highest as the acidity of HTA was pH2 from Fig. 4c.

3.4.3. Effect of HTA and NaOH's cleaning sequence

The effect of NaOH solution on the cleaning of WROM had been investigated, in which 6 mmol/L NaOH was the optimized result [35]. In order to make clear sequential order of HTA and NaOH solutions was what impact on the cleaning of ROM, the sequence test was conducted by using a 0.8% HTA and a 6 mmol/L NaOH as the cleanout liquid. In the process of the NaOH solution cleaning, use

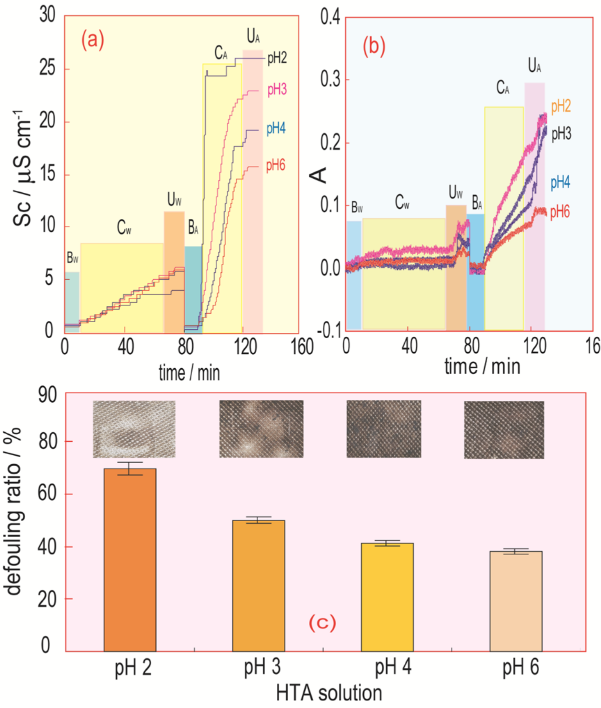

Fig. 4. Effects of pH in the HTA solution on organics (a) and descaling ratio (b) of ROM surfaces in different cleaning processes.

of the strong cation resin column was needed to decrease the blank conductivity of NaOH, in which its principle is shown in formulas 5–7 [45].

Sodium hydroxide ionization: $NaOH \rightarrow OH^- + Na^+$ (5)

Sodium hydroxide passing the cation resin column:
$RH + Na^+ \rightarrow RNa + H^+$ (6)

H^+ (from cation resin) + OH^- (from NaOH) →
H_2O (into the conductivity cell) (7)

In estimating the effect of base solution on the WROM cleaning, two processes were adopted, namely, $B_W \rightarrow C_A \rightarrow U_A \rightarrow B_W \rightarrow$ circulation cleaning of base solution (C_B) → ultrasonic-assisted base solution circulation cleaning (U_B) and $B_W \rightarrow C_B \rightarrow U_B \rightarrow B_W \rightarrow C_A \rightarrow U_A$, and the experiment result shown as Fig. 5 was obtained.

From a conductivity curve in Fig. 5a, it can be known that inorganic contaminants on the ROM surface washed with the HTA solution were more than one with the NaOH solution, and the reason may be that HTA reacts with some inorganic salts and transitional metal oxides to form soluble ions. Besides, the reason that the inorganic contaminant was washed off by NaOH may be because OH^- in sodium hydroxide can combine with Fe(III), Mn(II), Al(III), etc. to form precipitation, so circulating of the NaOH solution can also carry over some cation from the ROM surface.

Contrasting two absorbance curves in Fig. 5b, it can be seen that that HTA had significant effect to clean organic fouling on the ROM surface. This is because most of organic fouling all possesses carboxyl groups, which can form hydrogen bonds with HTA to enhance solubility of organic fouling, but the NaOH solution only enhances hydrophilicity of the ROM surface by changing the zeta potential, which can make a little organic fouling falling off from the ROM surface.

Fig. 5c indicated that all the ultrasonic-assisted acid or alkali solutions for the cleaning has a significant defouling effect on ROM, in which the defouling ratio obtained was 75.4% when the alkali cleaning was done after the HTA cleaning, if conversely, the descaling rate was increased to 79.4%. As a consequence, the procedure of the HTA cleaning after the alkali cleaning is beneficial for cleaning contaminants on the ROM surface. This conclusion can be applied to the cleaning process of ROM in water treatment industry.

3.4.4. Comparison of HTA with other acid and base in the cleaning effects

In this study, 0.8% HTA, 0.2% oxalic acid [46], 0.6% acetic acid, 1% citric acid [36], 0.24% hydrochloric acid, 0.5% phosphoric acid [23] and 0.24% NaOH and 0.6% KOH [35] were used as cleaning solutions to respectively contrast their cleaning effects for the ROM specimens. Fig. 6a displays that the cleaning effects of organic acids and inorganic acid (phosphoric acid) for inorganic on the ROM specimens were relatively good. Fig. 6b indicates that organic acids under ultrasound have all good effect in cleaning organics on the ROM specimens, in which efficacy of the HTA solution cleaning the organic fouling was be in middle. Fig. 6c also indicates that total defouling rate of organic acids was all the best.

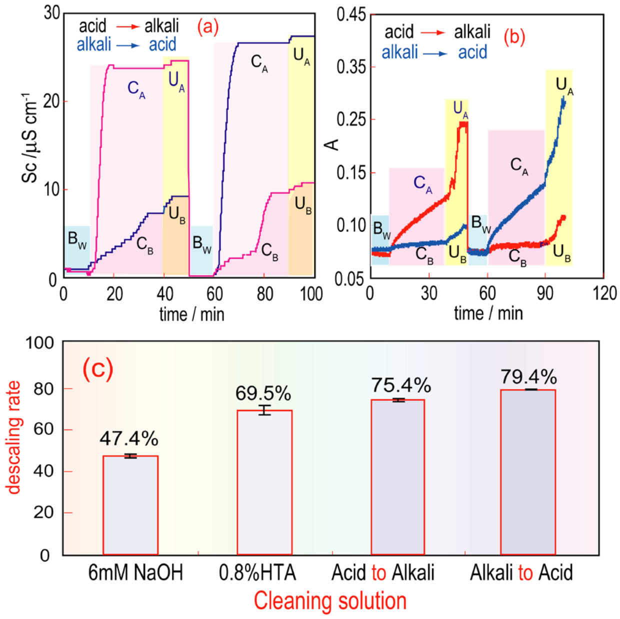

Fig. 5. Effects of acid and base cleaning order on inorganic (a) and organic (b) contaminants as well as defouling ratio (c) of ROM surfaces in different cleaning processes.

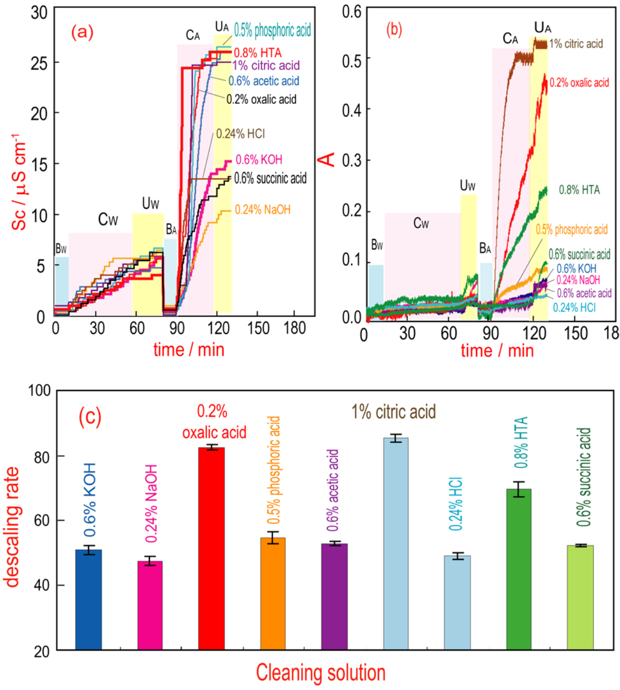

Fig. 6. Effect comparison of different acid and base used for cleaning ROM.

3.5. Compounding effect of HTA and Na_4EDTA

3.5.1. Influence of HTA/Na_4EDTA's mixing ratio on ROM cleaning

For purpose of further improving the cleaning efficacy of HTA, the research considered to conduct the compound cleaning for the ROM specimens, in which HTA was mixed with ethylenediaminetetraacetic acid disodium salt (Na_4EDTA) on the basis of the literatures screening [46]. Merit of using Na_4EDTA was that it can effectively remove divalent and trivalent metal cation and can be complexed with Ca^{2+} and Mg^{2+} in various pH ranges and various concentrations [41]. So, in the experiment, the cleaning capacity of eleven mixing solutions constituted by HTA and Na_4EDTA in different concentrations was appraised, in which ultrasound was also applied under the conditions of 50 kHz and 0.636 W/cm^2.

The ROM specimens with the same pollution degree were used as test samples to conduct the cleanout and ultrasonication, and the cleaning sequence of the HTA solution above-mentioned was adopted, that is, $B_W \rightarrow C_W \rightarrow U_W \rightarrow B_A \rightarrow C_A \rightarrow U_A$. Finally, the defouling ratios were calculated in the light of the ROM's mass change before and after cleaning, and the columnar graphs were gotten as shown in Fig. 7a. As you can see from this figure, when HTA mixed with Na_4EDTA by 0.8+1, 2+1, 3+1, 4+1, 5+1 and 6+1 ratios, namely, as the HTA content in the compound liquid gradually increased, the defouling ratio was enhanced, and as the mixed ratio between HTA and Na_4EDTA was 6+1, the defouling ratio could reach to 96% that is the largest. This indicated that HTA played a major role in the compound liquid under above mixing ratios. But, when HTA mixed with Na_4EDTA according to 7+1, 9+1, 11+1, 13+1 and 15+1 ratios, the defouling ratio started to gradually decrease, namely, as the relative content of Na_4EDTA was decreased, the defouling ratio for the ROM specimens went down. Consequently, from this, another conclusion can be obtained that the compound liquid of HTA and Na_4EDTA mixed by 6+1 ratio (6.9 g/L HTA + 1.1 g/L Na_4EDTA) can be used efficaciously for cleaning depth-fouled ROM in water treatment systems.

Whereafter, the water flux of the ROM specimens before and after cleaning was measured. The composition of the measurement system is shown in Fig. 7b. In measuring, a plunger pump pushes purified water into a clamper for fixing the ROM specimens, the purified water of passing through the ROM flows into a nether quantitative container, finally, the water flux is calculated according to the formula of $J = V A^{-1} t^{-1}$, where, the V is volume (100 mL) of the purified water penetrating the ROM specimens, A is the measured ROM area (13.85 cm^2), t is the time that collected a certain volume of the purified water which was passing through the ROM specimen. And then, the flux recovery rate of ROM is calculated according to $FR = J_1/J_0 \times 100\%$ formula, where J_1 is the water flux of the contaminated ROM before and after cleaning (L m^{-2} h^{-1}), and J_0 is the water flux of the same new ROM (L m^{-2} h^{-1}). The measurement results are shown in Fig. 7c. It can be seen that when the mixing ratio of the HTA and Na_4EDTA is 6+1, the water flux was also the largest, approaching 95%.

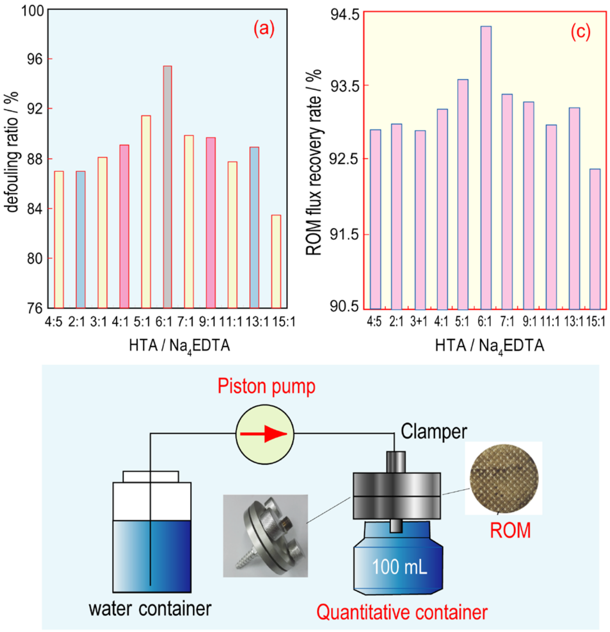

Fig. 7. Effects of the compounding ratios between HTA and Na_4EDTA on the defouling ratio of the ROM surface and measurement for the water flux of the ROM specimens.

3.5.2. SEM photos of ROM specimens before and after cleaning

In order to observe the cleanliness degree of the ROM specimens surface cleaned by using the HTA/Na_4EDTA compound liquid in the 6+1 ratio, the ROM surfaces were characterized by the SEM device, and the obtained photos are shown in Fig. 8, which exhibited the appearance from contaminant on the ROM surface under the same amplification multiples. The SEM images in Figs. 8a–c are virgin, fouled and cleaned ROM surfaces, respectively. Fig. 8b indicates that there were lots of contaminant on the ROM surface before cleaning, but when cleaned by the compound liquid, the surface of ROM was changed to be smooth and clean (Fig. 8c), which proved that mixing of HTA with Na_4EDTA had good cleaning effect to the ROM in the 6+1 ratio.

To further confirm the effect before and after cleaning for the ROM surface, the detection was conducted by the x-ray diffraction analyzer and the results were obtained as shown in Fig. 9. It can be also seen that the residual fouling on ROM surface was very little after the cleaning.

4. Conclusions

Main novelty in this research was as follows. (a). Using the self-designed and assembled ultrasonic cleaning and monitoring system for cleaning organic and inorganic pollutants on the ROM surface has realized the dynamic monitoring and real-time acquiring the relevant information; (b). The water flux measurement system self-designed was used to measure the flux changes before and after the ROM cleaning with different HTA/Na_4EDTA mixture, and to evaluate the recovery of ROM filtration performance according to

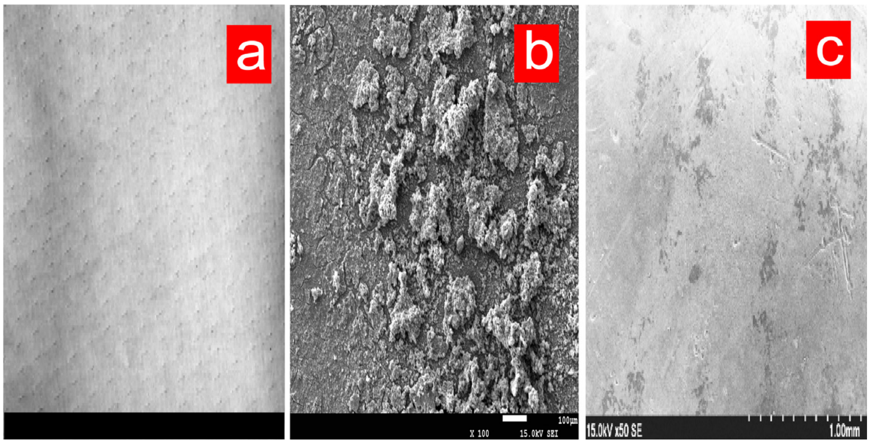

Fig. 8. Photographs on the ROM surface obtained by SEM. a, the new ROM; b, the polluted ROM; c, the cleaned ROM.

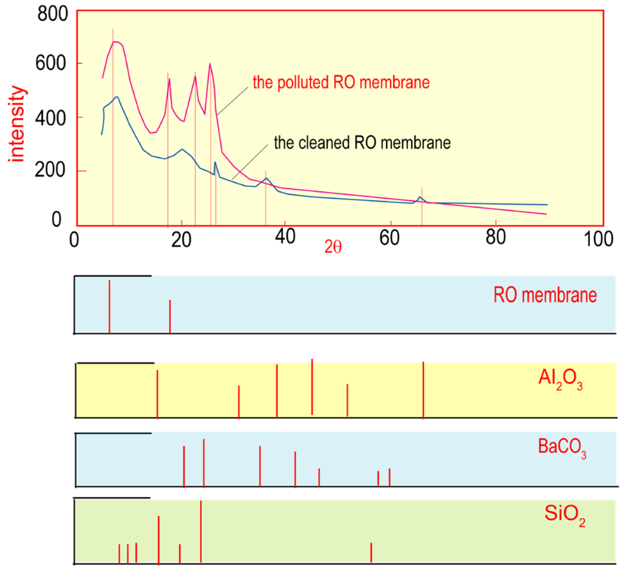

Fig. 9. XRD spectrum of contaminants on the ROM surfaces before and after the cleaning.

the obtained data. (c). For the first time, cleaning effects for the various combination and compound cleanings for ROM were evaluated, and a best cleaning process was obtained: water pre-cleaning under ultrasound-assisted → circulation cleaning of HTA/Na$_4$EDTA (6+1, *v/v*) compound liquid under ultrasound-assisted.

For the polyamide ROM depth-polluted by the transitional metal oxides of iron and manganese, aluminum, barium, calcium, silica and trace-level organic matters, the obtained research conclusion is that if only alone utilizing HTA, oxalic acid and citric acid to clean ROM, the defouling ratios can respectively reach about 70%, 83% and 85% under the ultrasound-assisted condition, and if adopting the process of the HTA cleaning after the NaOH cleaning, the defouling ratio can reach to 79.4%, and if using the mixture of 6.9 g/L HTA and 1.1 g/L Na$_4$EDTA to clean, the defouling ratio can reach to 96%, and the flux recovery rate of ROM could reach 94.3%, which is the best synergistic cleaning effect. The results coming from this research can be used for online cleaning the severely contaminated ROM in the industry water treatments.

Acknowledgement

Thanks to colleagues worked in the public instrument platform in School of Chemical Engineering, Sichuan University, for helping in the use of Fourier infrared spectrometer and scanning electron microscopy.

References

[1] H. Zeng, G. Zhang, Q. Meng, J. Chen, Q. Wang, Treatment of textile waste water using ultra filtration and reverse osmosis dual membrane system, Chinese J. Environ. Eng., 2 (2008) 1021–1025.

[2] J.H. Mo, Y.H. Lee, J. Kim, J.Y. Jeong, J. Jegal, Treatment of dye aqueous solutions using nanofiltration polyamide composite membranes for the dye wastewater reuse, Dyes Pigments, 76 (2008) 429–434.

[3] C. Fersi, L. Gzara, M. Dhahbi, Treatment of textile effluents by membrane technologies, Desalination, 185 (2005) 399–409.

[4] W.S. Ang, N.Y. Yip, A. Tiraferri, Chemical cleaning of RO membranes fouled by wastewater effluent: Achieving higher efficiency with dual-step cleaning, J. Membr. Sci., 382 (2011) 100–106.

[5] G. Intini, L. Liberti, UF and RO membrane fouling during wastewater desalination in the petrochemical industry, Desal. Water Treat., 57 (2016) 479–486.

[6] K. Kimura, D. Honoki, T. Sato, Effective physical cleaning and adequate membrane flux for direct membrane filtration (DMF) of municipal wastewater: Up-concentration of organic matter for efficient energy recovery, Sep. Purif. Technol., 181 (2017) 37–43.

[7] R. Shang, W.B.P. van den Broek, S.G.J. Heijman, S. van Agtmaal, L.C. Rietveld, Wastewater reuse through RO: a case study of four RO plants producing industrial water, Desal. Water Treat., 34 (2011) 408–415.

[8] A.H. Hashim, Flow transport modelling of feed species (water and salt) through a seawater RO membrane, Desal. Water Treat., 51 (2013) 1385–1404.

[9] R.Y. Ning, A.J. Tarquin, J.E. Balliew, Seawater RO treatment of RO concentrate to extreme silica concentrations, Desal. Water Treat., 22 (2010) 286–291.

[10] H.-M. Ruan, J.-H. Qiu, J.-N. Shen, Study on the cleaning of seawater reverse osmosis polyamide membranes, Tech. Water Treat., 34 (2008) 47–49.

[11] S.B. Lee, Y.J. Kim, A.S. Kim, S.K. Hong, Evaluation of membrane-based desalting processes for RO brine treatment, Desal. Water Treat., 57 (2016) 7432–7439.

[12] M. Turek, J. Was, P. Dydo, Brackish water desalination in RO–single pass EDR system, Desal. Water Treat., 7 (2009) 263–266.

[13] N. Afrasiabi, E. Shahbazali, RO brine treatment and disposal methods, Desal. Water Treat., 35 (2011) 39–53.

[14] B. Garcia-Fayos, J.M. Arnal, A. Gimenez, Optimization of chemical cleaning of a reverse osmosis membrane from a desalination plant by means of two-step static tests, Desal. Water Treat., 55 (2015) 3367–3379.

[15] S.S. Madaeni, A. Sasanihoma, S. Zereshki, Chemical cleaning of reverse osmosis membrane fouled by apple juice, J. Food Process Eng., 34 (2011) 1535–1557.

[16] S.S. Madaeni, A. Sasanihoma, S. Zereshki, Chemical cleaning of reverse osmosis membrane fouled by sugar solution, Asia-Pac. J. Chem. Eng., 5 (2010) 691–700.

[17] S. Jamaly, N.N. Darwish, I. Ahmed, S.W. Hasan, A short review on reverse osmosis pretreatment technologies, Desalination 354 (2014) 30–38.

[18] M. Pontie, Old RO membranes: solutions for reuse, Desal. Water Treat., 53 (2015)1492–1498.

[19] H.D. Raval, V.R. Chauhan, A.H. Raval, S. Mishra, Rejuvenation of discarded RO membrane for new applications, Desal. Water Treat., 48 (2012) 349–359.

[20] A. Ambrosi, I.C. Tessaro, Study on potassium permanganate chemical treatment of discarded reverse osmosis membranes aiming their reuse, Sep. Sci. Technol., 48 (2013) 1537–1543.

[21] S.S. Madaeni, T. Mohamamdi, M.K. Moghadam, Chemical cleaning of reverse osmosis membranes, Desalination, 134 (2001) 77–82.

[22] S.S. Madaeni, S. Samieirad, Chemical cleaning of reverse osmosis membrane fouled by wastewater, Desalination, 257 (2010) 80–86.

[23] J.-Y. Yang, Y.-S. Li, B. Huang, Research on refurbishing of the used RO membrane through chemical cleaning and repairing with a new system, Desalination, 320 (2013) 49–55.

[24] K.L. Tu, A.R. Chivas, L.D. Nghiem, Chemical cleaning effects on properties and separation efficiency of an RO membrane, Membr. Water Treat., 6 (2015) 141–160.

[25] E. Filloux, J.S. Wang, M. Pidou, Biofouling and scaling control of reverse osmosis membrane using one-step cleaning-potential of acidified nitrite solution as an agent, J. Membr. Sci., 495 (2015) 276–283.

[26] W.S. Ang, S.Y. Lee, M. Elimelech, Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes, J. Membr. Sci., 272 (2006) 198–210.

[27] H.-G. Li, P. Yu, Y.-B. Luo, Oxidative cleaning of reverse osmosis membranes during reclamation of steel wastewater, Desal. Water Treat., 57 (2016) 5687–5699.

[28] A.B. Alayande, L.H. Kim, I.S. Kim, Cleaning efficacy of hydroxypropyl-beta-cyclodextrin for biofouling reduction on reverse osmosis membranes, Biofouling, 32 (2016) 359–370.

[29] O. Krasulya, S. Shestakov, V. Bogush, I. Potoroko, P. Cherepanov, B. Krasulya, Applications of sonochemistry in Russian food processing industry, Ultrason. Sonochem., 21 (2014) 2112–2116.

[30] P. Srivastava, S. Goyal, P.K. Patnala, Degradation of reactive, acid and basic textile dyes in the presence of ultrasound and rare earths [Lanthanum and Praseodymium], Ultrason. Sonochem., 21 (2014) 1994–2009.

[31] P.B. Subhedar, P.R. Gogate, Ultrasound-assisted bioethanol production from waste newspaper, Ultrason. Sonochem., 27 (2015) 37–45.

[32] J. Llanos, S. Cotillas, P. Cañizares, M.A. Rodrigo, Conductive diamond sono-electrochemical disinfection (CDSED) for municipal wastewater reclamation, Ultrason. Sonochem., 22 (2015) 493–498.

[33] D. Cranston, A review of high intensity focused ultrasound in relation to the treatment of renal tumours and other malignancies, Ultrason. Sonochem., 27 (2015) 654–658.

[34] H. Liu, Y. He, J. Shao, Applications and recent advances of ultrasound as a membrane cleaning technique, Membr. Sci. Technol., 5 (2006) 158–162.

[35] J.-G. Huang, Y.-S. Li, J.-Y. Yang, Effect of alkaline solution and ultrasonic for efficiency of cleaning pollutants on the RO membrane surface, J. Sichuan Univ. (Eng. Ed.), 45 (2013) 128–132.

[36] Y.-S. Li, L.-C. Shi, X.-F. Gao, J.-G. Huang, Cleaning effects of oxalic acid under ultrasound to the used reverse osmosis membranes with an online cleaning and monitoring system, Desalination, 390 (2016) 62–71.

[37] J. Wang, X.-L Gao, Y. Xu, Q. Wang, Y.-S. Zhang, X.-Y. Wang, C.-J. Gao, Ultrasonic-assisted acid cleaning of nanofiltration membranes fouled by inorganic scales in arsenic-rich brackish water, Desalination, 377 (2016) 172–177.

[38] J.-X. Li, R.D. Sanderson, E.P. Jacobs, Ultrasonic cleaning of nylon microfiltration membranes fouled by Kraft paper mill effluent, J. Membr. Sci., 205 (2002) 247–257.

[39] D. Feng, J.S.J. van Deventer, C. Aldrich, Ultrasonic defouling of reverse osmosis membranes used to treat wastewater effluents, Sep. Purif. Technol., 50 (2006) 318–323.

[40] C.G. Kim, T. Yoon, M.J. Lee, Characterization and control of foulants occurring from RO disc-tube-type, membrane treating, fluorine manufacturing, process wastewater, Desalination, 151 (2002) 283–292.

[41] Y. Xiao, T. Chen, Y. Hu, D. Wang, Y. Han, X. Wang, Fouling characteristic of RO membrane in the semiconductor wastewater reclamation by using MBR-RO process, Technol. Water. Treat., 39 (2013) 53–58.

[42] Y.-S. Li, Y.-L. Dong, Determination of anion exchange resin performance based on facile chloride-ion monitoring by FIA-spectrophotometry with applications to water treatment operation, Anal. Sci., 20 (2004) 831–836.

[43] W. Jin, Y. He, J. Shao, Studies on the UV (254_{nm}) absorbance as a surrogate parameter of organic matter, Ind. Water. Treat., 17 (1997) 30–32.

[44] E. Ou Yang, X. Zhang, Z. Zheng, On-line raw water quality detection with UV organics analysis, Environ. Sci. Technol., 29 (2006) 39–42.

[45] Y.-S. Li, H. Guo, Determination method for exchange capacity of cation exchange resins based on flow-injection ion-selected electrode, Chin. J. Anal. Chem., 36 (2008) 805–810.

[46] L.-C. Shi, Y.-S. Li, X.-F. Gao, Online monitoring of organic pollutants and inorganic ion contents in the process of reverse osmosis membrane cleaning, Chin. J. Anal. Lab., 35 (2016) 841–845.